



Beneficial effects of activated carbon additives on the performance of negative lead-acid battery electrode for high-rate partial-state-of-charge operation



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HIGHLIGHTS

- We report a 12 V Pb–C battery with as-designed activated carbon in NAM.
- Carbon additives optimize NAM microstructure and enhance electrode reaction kinetics.
- The battery exhibits more than 110,000 cycles under HRPSoC condition.
- The battery exhibits 20% improved charge acceptance comparing to the common one.
- Carbon acts as porous-skeleton builder, electrolyte supplier and capacitive buffer.

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ABSTRACT

Experiments are made with negative electrode of 2 V cell and 12 V lead-acid battery doped with typical activated carbon additives. It turns out that the negative electrode containing tens-of-micron-sized carbon particles in NAM exhibits markedly increased HRPSoC cycle life than the one containing carbon particles with much smaller size of several microns or the one containing no activated carbon. The improved performance is mainly attributed to the optimized NAM microstructure and the enhanced electrode reaction kinetics by introducing appropriate activated carbon. The beneficial effects can be briefly summarized from three aspects. First, activated carbon acts as new porous-skeleton builder to increase the porosity and active surface of NAM, and thus facilitates the electrolyte diffusion from surface to inner and provides more sites for crystallization/dissolution of lead sulfate; second, activated carbon plays the role of electrolyte supplier to provide sufficient H_2SO_4 in the inner of plate when the diffusion of H_2SO_4 from plate surface cannot keep pace of the electrode reaction; Third, activated carbon acts as capacitive buffer to absorb excess charge current which would otherwise lead to insufficient NAM conversion and hydrogen evolution.

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1. Introduction

The environment concerns over the use of fossil fuels and their resource constraint have spurred great interest in low-emission transport like electric vehicles, and also the wind/solar energy storage and utilization. No matter in hybrid electric vehicles (HEV) or in intermittent energy storage systems, the battery has to operate continuously at partial-state-of-charge (PSoC) duty and accept charge at extremely high rates when vehicle braking or wind is heavy. In addition, high-rate discharge is necessary for engine

cranking and power-assist. That is, the battery is said to undergo high-rate partial-state-of-charge duty (HRPSoC) [1,2]. However, under such a duty, conventional lead-acid batteries, such as those designed for SLI (starting, lighting and ignition) or deep-cycle use, would quickly accumulate lead sulfate on the surface of negative plate [3], which cannot be converted efficiently back to spongy lead during charge, then thus limit the cycle life of the batteries.

Therefore, the lead-acid battery developed over decades for SLI duty, telecommunications or UPS applications must be modified significantly in order to provide the power capability and adequate service-life demanded by future automobile electrical systems and energy storage systems. The key objective is to overcome the processes that give rise to the accumulation of sulfate on the negative plate in HRPSoC duty.

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Table 1
Characteristics of carbon additives under investigation.

Type of material	Mean particle size (D_{50} , μm)	BET surface ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Average pore size (nm)	Capacitance under 0.05 A g^{-1} (F g^{-1})	Conductivity (S cm)
Activated carbon 1#	4.0	1156	0.615	2.12	249	0.33
Activated carbon 2#	68.0	2826	1.662	2.35	367	0.34
Graphite	18.5	7.4	0.042	22.73	—	82.33

Nakamura, Shiomi and co-authors [4,5] have established that introduction of carbon black to the negative active material (NAM) retards substantially the sulfation of the negative plates during the simulated HRPSoc test of batteries for HEV applications. Newnham et al. [6] have found that the specific surface area of NAM is an important parameter as it sustains the potential of the negative plates below the hydrogen evolution potential. In recent years, it is widely accepted that incorporation of elevated concentration of carbon (a few wt.% instead of the traditional 0.2 wt.%) is a promising route to alleviate the tendency for sulfate accumulation and possesses a long operating life in HRPSoc duty [7–11]. The types of carbon additives could be carbon black, activated carbon, graphite, or mixture of them. Micka's group [12,13] has pointed out that the effect of carbon is due to steric hindrance of the sulfate crystallization rather than the electric conductivity of graphite via investigating HRPSoc cycle life of the negative plate not only by adding graphite but also adding isolated titanium dioxide. Pavlov and co-workers [8] have established that, during cycling of cells under HRPSoc condition, the electrochemical reactions of charge at the negative plates occur not only on the lead sulfate, but on the surface of the carbon as well. They proposed a parallel electrochemical mechanism of charge and came to the conclusion that carbon must be incorporated in and impact the structure of NAM to influence the battery performance under HRPSoc duty [14].

The main possible functions of carbon additives to negative plate performed in HRPSoc cycling have been summarized by P.T. Moseley [15]: (i) enhancing the overall electrical conductivity of NAM; (ii) restricting lead sulfate crystal growth; (iii) absorbing excess charge current as a capacitor; (iv) reducing the hydrogen over-potential and thus facilitating hydrogen emission. However, not all carbon forms that exhibit high conductivity or increase the specific surface area of NAM could be favorable for battery cycle life under HRPSoc operation [7]. So far, the optimum type of carbon additives and actual effect mechanism for improved HRPSoc cycling performance of lead-acid batteries are still unclear and need further investigation.

In the present work, we prepare two groups of possible suited activated carbon materials, and add them to the negative plate. The HRPSoc cycling performance, charge acceptance ability and other properties of Pb–C negative plate are evaluated in both simulated 2 V test cells and 12 V batteries. The correlation between electrochemical properties of cells/batteries and microstructures of NAM is paid close attention. The aim of the present investigation is to disclose the positive function mechanism of activated carbon additives on the electrochemical processes of the negative plate in HRPSoc duty.

2. Plate preparation and battery design

2.1. Carbon materials added to NAM

The as-prepared carbon additives were of very high active surface area and different particle size range from several microns to tens of microns. Graphite with much low BET surface but relative high electrical conductivity was also selected for

comparison. The characteristics of carbon additives are summarized in Table 1.

2.2. Negative paste preparation and characterization

Experimental groups of carbon additives doped to negative pastes are listed in Table 2. Paste without carbon was also prepared and used for assembling reference plates. All the plates were cured and dried at 65°C for 24 h.

The samples of NAM after formation and HRPSoc cycling were characterized by scanning electron microscope (SEM, Hitachi S-3400N) and BET Surface Analyzer (Gemini VII 2390).

2.3. Simulated test cell and battery design

The influence of carbon additives on the performance of negative lead-acid battery plate was investigated both in 2 V simulated test cells and 12 V batteries.

The design characteristics of 2 V simulated test cells are presented in Table 3. Before cell assembly, the negative plates were formed in 1.04 sp. gr. H_2SO_4 . The process of formation composes of a charge at 0.22 C_{10} for 10 h, a discharge at 0.1 C_{10} for 0.5 h and a further charge at 0.2 C_{10} for 10 h. In each 2 V test cell, one negative plate was assembled with two positive plates, and AGM separator (Sinoma International) with a thickness of 1.65 mm at 10 kPa (93% porosity) were used at 25% compression. The cells were filled with H_2SO_4 of 1.304 sp. gr. and sealed. 12 V Prototype battery with 20-h capacity of 75 A h was also produced as shown in Fig. 1. For contrast, 2 V cell and 12 V battery consisted of same positive and negative plates without carbon additives were also produced.

3. Electrochemical performances of test cells and batteries

3.1. Simplified HRPSoc cycling

The effects of carbon materials on HRPSoc performance were evaluated in simulated test cell using a simplified profile imitating the micro-hybrid driving mode. The first step in this cycling profile was discharging at 1 C rate to 50% SoC. After that, the cells were subjected to cycling according to the following procedures: charge at 2 C rate for 90 s (upper voltage limit of 2.54 V), rest for 10 s, discharge at 2 C rate for 60 s, rest for 10 s. The cell voltage was measured at the end of the discharge pulses and the test was stopped when the cell discharge voltage fell down to 1.70 V.

Table 2
Experimental groups of carbon additives to negative plate.

Signature	Composition	Concentration in NAM (wt.%)
Ref	—	—
AC1	Activated carbon 1#	2%
AC2	Activated carbon 2#	2%
AG	Activated carbon 2# + graphite	1% + 1%

Table 3
Simulated test cell design characteristics.

	Negative plate	Positive plate
Grid alloy	Pb–Ca	Pb–Sn–Ca
Grid thickness (mm)	1.5	1.5
Grid dimensions (mm × mm)	65 × 39	65 × 39
Plate per cell	1	2
Plate thickness (mm)	2.0	2.4

The results of simplified HRPSoc cycling were shown in Fig. 2. The reference, AC1 and AC2 cells reached the end of their lives at about 7000, 10,700 and 15,600 cycles, respectively. Obviously, the cell with 2 wt.% activated carbon prolongs the cycle life under the accelerated HRPSoc regime. Moreover, the activated carbon with tens of microns in diameter exhibits more visible improvement than the one with size of only several microns.

The cell voltage and electrode potentials of the test cells in a typical HRPSoc cycle without upper voltage limitation are recorded in Fig. 3. With activated carbon in NAM, the end-of-charge potential of negative plate increases from -1.6 V to -1.1 V, and the discharge potential decreases about 50 mV. As can be seen, activated carbon loaded in NAM brings to the decreasing polarization of the negative plate, especially during the late stage of charge. This behavior is similar to the observation of Pavlov et al. [8] who found a distinct electrocatalytic effect of active carbon on the cathodic reduction of lead sulfate. Besides, the electrocatalytic effect of activated carbon with tens of microns in size is much more notable, of which the cell delivers the longest HRPSoc cycle life as displayed in Fig. 2.

3.2. HRPSoc cycling for energy-recovery application

The HRPSoc cycling performances of 12 V batteries were evaluated using a profile to imitate the lifting and landing conditions of port crane. First, discharge battery with 0.1 C (7.5 A) for 3 h to 70% SoC; second, 2 C (150 A) charge for 16 s with 14.4 V limited upper voltage imitating the lifting process, rest for 5 s, 1.7 C (125 A) discharge for 15 s imitating the landing process, rest for 5 s, repeat these steps for 20 cycles, then rest for 2780 s; third, repeat the second procedure for 700 cycles which is equivalent to one-month calendar life, then fully charge battery to 13.5 V per block under 0.1 C within 24 h; last, repeat the above procedures until reaching to the cut-off voltage of 10.5 V.

The cycling performance of the 12 V Pb–C battery with AC2 negative plate under port-crane profile is presented in Fig. 4. The 12 V Pb–C battery has cycled up to more than 110,000 cycles and is still in healthy condition. The Pb–C battery shows much longer life



Fig. 1. Appearance of prototype 12 V Pb–C battery.

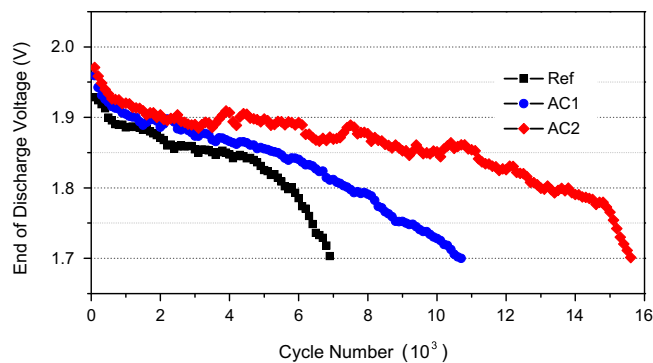


Fig. 2. HRPSoc cycling performance of test cell groups under a simplified profile imitating the micro-hybrid driving mode.

than the VRLA battery superimposed with high-frequency pulses, which was developed previously in the CSIRO laboratories (e.g. 42,000 cycles [16]). It is also indicated the promising potential of Pb–C battery for energy-recovery application.

3.3. Low-temperature capacity and charge acceptance

The capacities of 12 V batteries were tested at temperature of -10 °C to determine the effects of carbon additives on the low-temperature performance. AC2 and reference battery exhibit capacity of 27.82 A h and 23.74 A h after discharged at C_3 to the cut-off voltage of 4.2 V, respectively. The as-given capacity is an average value of five test batteries for each type.

The evaluation of charge acceptance of the battery proceeds as follows: (i) discharge the battery with 0.1 C to 50% SoC; (ii) rest for 24 h at temperature of 0 °C; (iii) charge the battery with constant voltage of 14.4 V and no current limitation; (iv) record the current I' as charged for 10 min, and calculate the ratio of I'/I^0 (I^0 is 10 h-rate current). As shown in Fig. 5, the I'/I^0 value of AC2 battery is almost 20% higher than that of the reference one. Higher I'/I^0 value indicates better charge acceptance. The improved low-temperature capacity and charge acceptance indicate the porosity of NAM must be highly increased and the electrolyte diffusion is greatly enhanced by adding activated carbon in negative plate.

According to the above results, it can be concluded that with micro-sized activated carbon particles in NAM, the negative plate is significantly depolarized, and the cell exhibits much longer HRPSoc cycle life and greatly enhances charge acceptance.

4. The functions of micro-sized activated carbon on improved HRPSoc performance

4.1. New porous-skeleton builder

The morphology of the referenced, AC1 and AC2 pastes after formation is presented in Fig. 6. The referenced paste comprises of homogeneous spongy Pb. For AC1 paste, since the size of AC1 is several microns, similar to that of Pb particles, AC1 additives disperse well among the spongy Pb. For AC2 paste, it comprises of large activated carbon particles and relative small Pb particles, where AC2 acts as frames and Pb particles contact well with them.

BET surface of formed negative paste is measured by N_2 absorption method. According to the results presented in Table 4, the BET surface area of NAM is significantly increased from $0.522 \text{ m}^2 \text{ g}^{-1}$ to $25.408 \text{ m}^2 \text{ g}^{-1}$ and $55.406 \text{ m}^2 \text{ g}^{-1}$ by introducing AC1 and AC2 activated carbons, respectively. The greatly increased BET surface area is partially attributed to the large surface area of

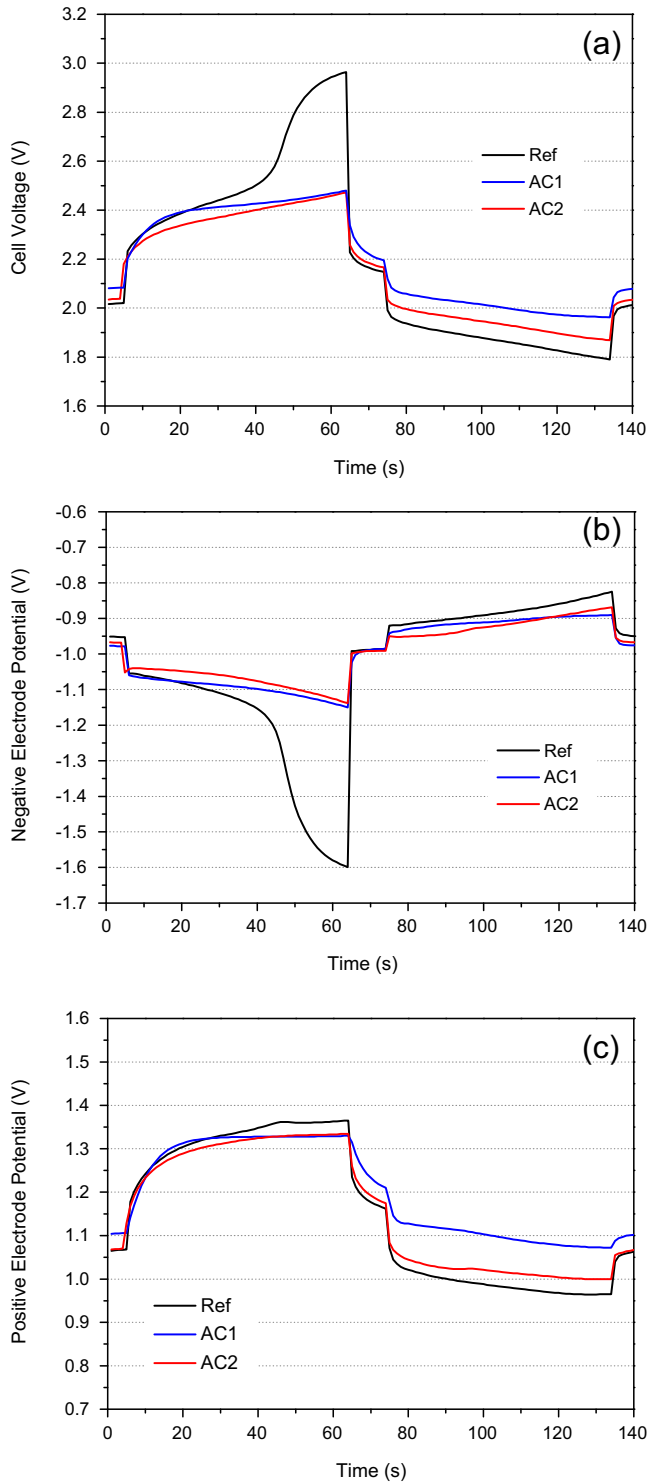


Fig. 3. Cell voltage and electrode potentials of 2 V test cells in one HRPSoC cycle: (a) cell voltage; (b) negative electrode potential; (c) positive electrode potential.

mesopores in activated carbon. However, the effect of activated carbon on the microstructure of NAM cannot be ignored, which is manifested in the total pore surface values measured by Hg penetration method (Table 4). Generally, the pore measure range of Hg penetration is 50 nm to 360 μm , thus it can eliminate the surface contribution of mesopores in activated carbon. As can be seen, the micro-sized pore area of AC1 and AC2 paste is $0.953 \text{ m}^2 \text{ g}^{-1}$ and $0.995 \text{ m}^2 \text{ g}^{-1}$ respectively, which is also a little larger than that of

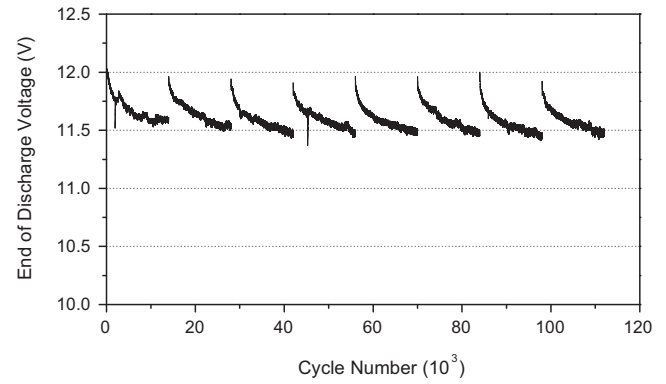


Fig. 4. HRPSoC cycling performance of 12 V Pb-C battery under a profile to imitate the lifting and landing duty for port-crane application.

the reference one ($0.508 \text{ m}^2 \text{ g}^{-1}$). Moreover, the porosity of NAM rises from 40.2% to 51.2% and 56.6% after introducing AC1 and AC2 activated carbons, respectively. Therefore, it is considered the activated carbons in negative plate serve as “expanders” that increase the porosity and BET surface of NAM. Moreover, the “expanding effect” of AC2 is more notable than that of AC1, owing to the larger particle size of AC2 that build the more loose and porous structure.

To deserve to be clarified, the “expanding effect” of activated carbons is different from that of carbon black additive. In conventional lead acid batteries, carbon black added into NAM acts as surfactant to redistribute the absorption state of active groups of organic expanders like OH^- , COH , SO_3 , facilitate the dissolution of PbSO_4 , and thus enhance the charge acceptance ability. The amount of carbon black is very small ($\sim 0.2 \text{ wt.}\%$), otherwise it will deteriorate the performance. But for activated carbon additives with size of tens of microns, they act as rigid frames to support a 3D network, which separate active materials, prevent the shrinkage of spongy lead, provide larger active surface area for lead sulfate crystallization and dissolution, and thus enhances the charge acceptance and HRPSoC cycling performance.

Figs. 7 and 8 show the morphology of NAM across the cross-section of reference and AC2 cycled negative plates, respectively. In the cycled reference negative plate, the particles accumulated on the surface with size of 5–10 μm is PbSO_4 , and the smaller particles in the interior with size of 2–3 μm is Pb. That is to say, lead sulfate

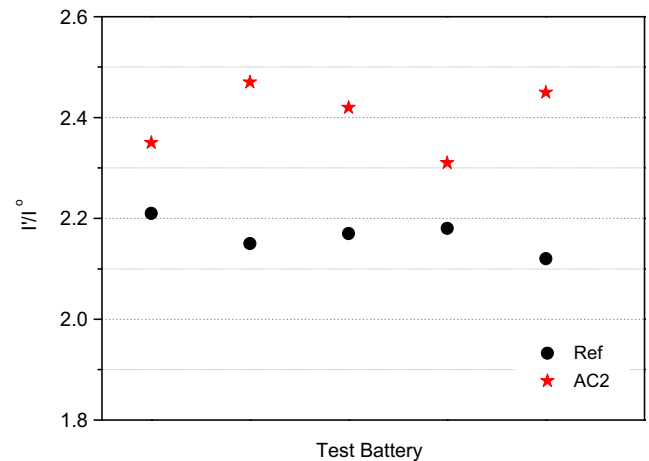


Fig. 5. Charge acceptance of 12 V battery at low temperature (five test batteries for reference and AC2 type, respectively).

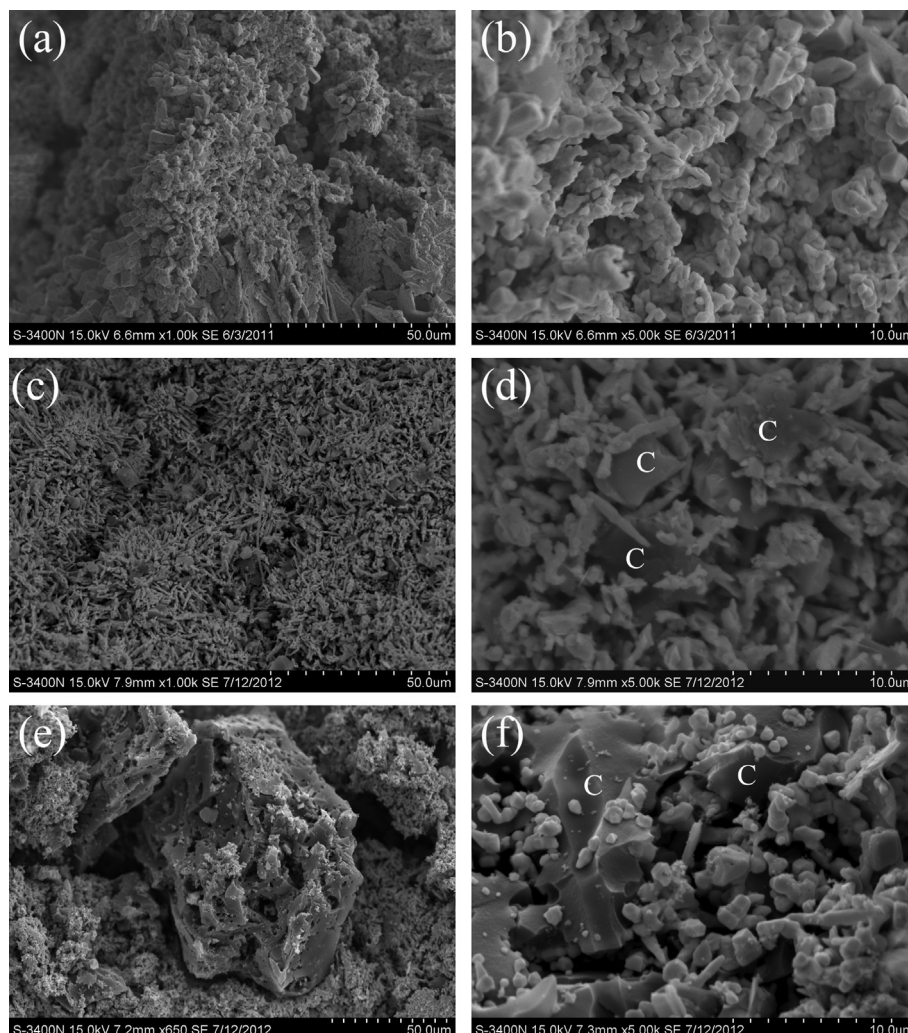


Fig. 6. SEM images of formed NAM: (a) and (b) reference; (c) and (d) AC1; (e) and (f) AC2.

deposits mainly on the faces of reference plate, adjacent to the bulk electrolyte and little presents in the interior. However, for the cycled Pb–C negative plate, the large particles on the surface and in the interior show the similar structure and morphology, which means the uniform distribution of PbSO_4 across the cross-section of the negative plate. PbSO_4 is formed throughout the entire cross-section of the Pb–C plate indicates the increasing porosity of NAM by adding carbon particles with size of tens of microns, which is consistent with the expanding effect mechanism of activated carbon additives as discussed above.

4.2. Inner electrolyte supplier

Activated carbon additives can not only increase the micropore volume in NAM, but also lead large number of mesopores as shown in Table 5. Hg intrusion volume indicates the micropore volume in

negative paste which measured by Hg penetration method. Mesopore volume in carbon is calculated according to the pore volume of carbon in Table 1 measured by BET analyzer. Mesopore/micropore volume ratio of AC1 and AC2 paste is 7.2% and 17.7%, respectively. These figures give us reason to believe that some other mechanisms may operate except for “expanding effect”. The electrode reaction kinetics process needs further investigation.

For regular negative plate, charging of the plate proceeds through the following “dissolution–crystallization” processes: (i) dissolution of PbSO_4 crystals; (ii) diffusion of the formed Pb^{2+} ions to the metal surface; (iii) electron transfer from the metal surface to Pb^{2+} ions and formation of Pb atoms; (iv) surface diffusion of Pb atoms to lead growth fronts and incorporation of these atoms into the growing Pb crystal lattice. Conversely, the discharge process includes the steps of electrochemical dissolution of Pb to Pb^{2+} and chemical crystallization of PbSO_4 . If any of the above elementary processes is impeded, the whole charge or discharge process is retarded. During HRPSoC cycling, the discharge cannot proceed into the interior of the plate, but stops at the surface, since the diffusion of H_2SO_4 from plate surface to inner cannot keep pace of the transfer of electrons. Thus the utilization of the active material is low. Consequently, the relative density of the acid after discharge is still at a high level and it decreases the dissolution of PbSO_4 . The lower concentration of Pb^{2+} will then impede the subsequent

Table 4
BET surface and porosity of NAM for each test group.

Group	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Pore area ($\text{m}^2 \text{g}^{-1}$)	Porosity (%)
Ref	0.522	0.508	40.2
AC1	25.408	0.953	51.2
AC2	55.406	0.995	56.6

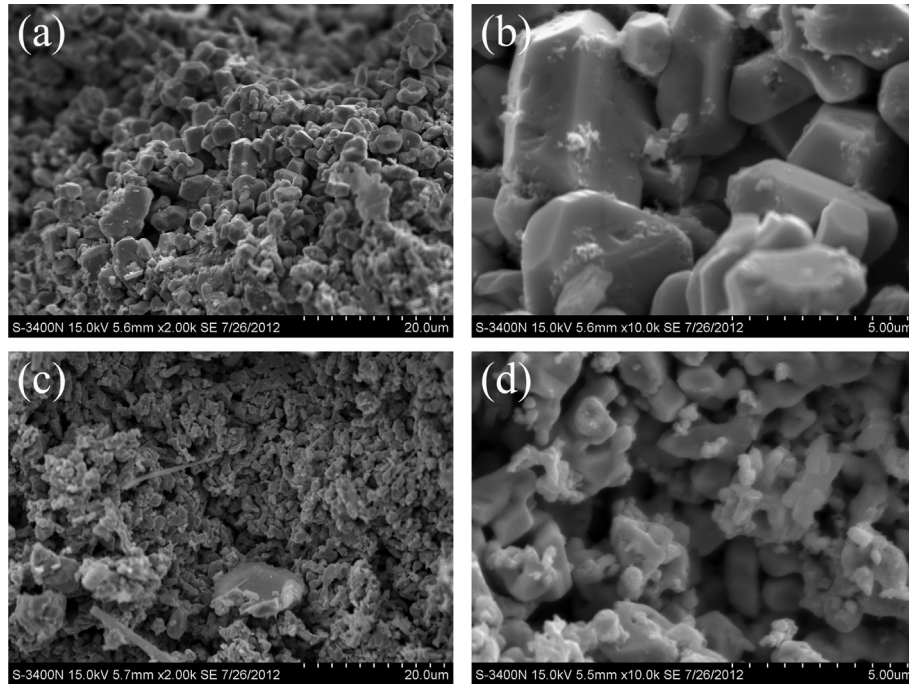


Fig. 7. SEM images of HRPSoc cyclized NAM across the cross-section of reference negative plates: (a), (b) surface and (c), (d) interior.

electrochemical reaction from Pb^{2+} to Pb, and cause the negative-plate potential to become more negative to such extent that hydrogen can start to evolve [3]. Thus, lead sulfate will accumulate on the surface of the negative plate with increasing cycling, and the battery will be failed eventually.

Adding activated carbon particles into NAM would make the electrode reaction kinetics process quite different. As mentioned above, AC1 and AC2 exhibit high pore volume of $0.615 \text{ cm}^3 \text{ g}^{-1}$ and

$1.662 \text{ cm}^3 \text{ g}^{-1}$, and mean porous diameter of about 2 nm. The radii of H_3O^+ and HSO_4^- is generally considered as about 200–400 pm [17,18], much less than the mesopore size of activated carbon. The large pore volume of activated carbon provides a great number of sites for H_2SO_4 accommodation. In other words, micro-sized activated carbon particles serve as large H_2SO_4 receptacles in the interior of negative plate, and supply H^+ and HSO_4^- as much as necessary. The schematic diagram for electrolyte-supplying effect

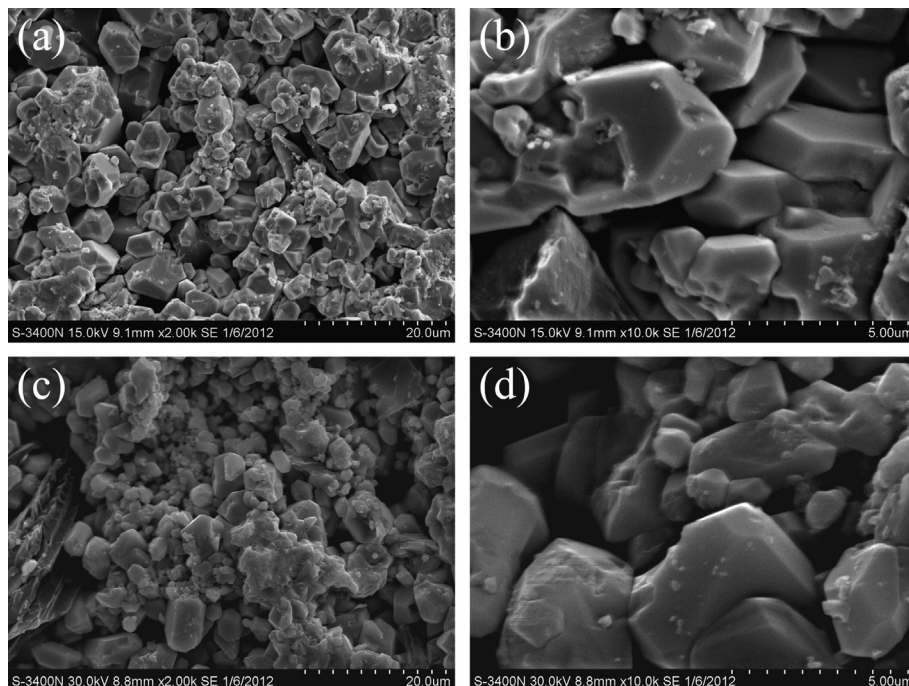


Fig. 8. SEM images of HRPSoc cyclized NAM across the cross-section of AC1 negative plates: (a), (b) surface and (c), (d) interior.

Table 5
Pore volume analysis of NAM for each test group

Group	Hg intrusion volume ($\text{cm}^3 \text{g}^{-1}$)	Mesopore volume in carbon ($\text{cm}^3 \text{g}^{-1}$)	Mesopore/micropore volume ratio
Ref	0.1149	—	—
AC1	0.1709	0.0123	7.2%
AC2	0.1880	0.0332	17.7%

of activated carbons is presented in Fig. 9. During high rate discharge, the reaction would no longer stop at the surface, but proceed into the interior of plate, since the sufficient H_2SO_4 released from the microspores of activated carbon particles in the inner. As a result, lead sulfate is formed throughout the entire cross-section of the plate and the relative density of the acid after discharge is low because of the high utilization of the active material. The dissolution of PbSO_4 to form Pb^{2+} and SO_4^{2-} increases at the low concentrations. Thus, the subsequent reduction of Pb^{2+} to sponge lead can take place smoothly before the evolution of hydrogen.

In brief, the micro-sized activated carbon cooperate well with spongy Pb in the negative electrode: Pb particles act as electrical conductive network offering fast electron transferring channels for electrochemical dissolution ($\text{Pb} \rightarrow \text{Pb}^{2+}$) and electrochemical crystallization ($\text{Pb}^{2+} \rightarrow \text{Pb}$) during discharge and charge processes, and micro-sized activated carbon particles act as an inner electrolyte-supplier providing efficient HSO_4^- and H^+ for chemical crystallization ($\text{Pb}^{2+} \rightarrow \text{PbSO}_4$) and chemical dissolution ($\text{PbSO}_4 \rightarrow \text{Pb}^{2+}$) during HRPSoC cycling.

It is worth mentioning that the electronic conductivity of activated carbon with high surface area is lower than that of the

principle active material of negative plate (metallic Pb), however, the conductance test results of the entire Pb–C batteries is beyond our expectation (Fig. 10). As can be seen, activated carbon added into negative plate would cause no adverse but beneficial effects to the conductance of the negative electrode (the measurement is under fully-charged state). The conductance improvement is not absolutely proportional to the electronic conductivity of the carbon additives. For instance, the electronic conductivity of AG is better than that of AC2, but the conductance of the AG battery is less than that of the AC2 battery. Therefore, it is supposed that the improved conductance is with less relationship to the conductivity of the carbon additive, but greatly influenced by the increasing porosity and facilitated electrolyte diffusion after introducing carbon in NAM.

4.3. Capacitive buffer

Ultrabattery, developed by CSIRO Energy Technology and the Furukawa Battery Co., Ltd., combines an asymmetric supercapacitor and a lead-acid battery in a unit cell [19]. It is widely considered the capacitor electrode containing a mixture of carbon black and activated carbon acts as a buffer to share the discharge and charge currents with the lead-acid negative plate, and thus prevent it from being discharged and charged at high rate. Is it then possible that the capacitive effect still function in Pb–C negative plate where activated carbon particles mixed into spongy Pb active materials?

Before investigating the capacitive function of activated carbon in NAM, we firstly connected a “lead cell” (one Pb negative plate and two PbO_2 positive plates) and a “carbon cell” (one AC2 negative plate and two PbO_2 positive plates) in parallel, and test the current flowing through the two cells, respectively. The shape and size of

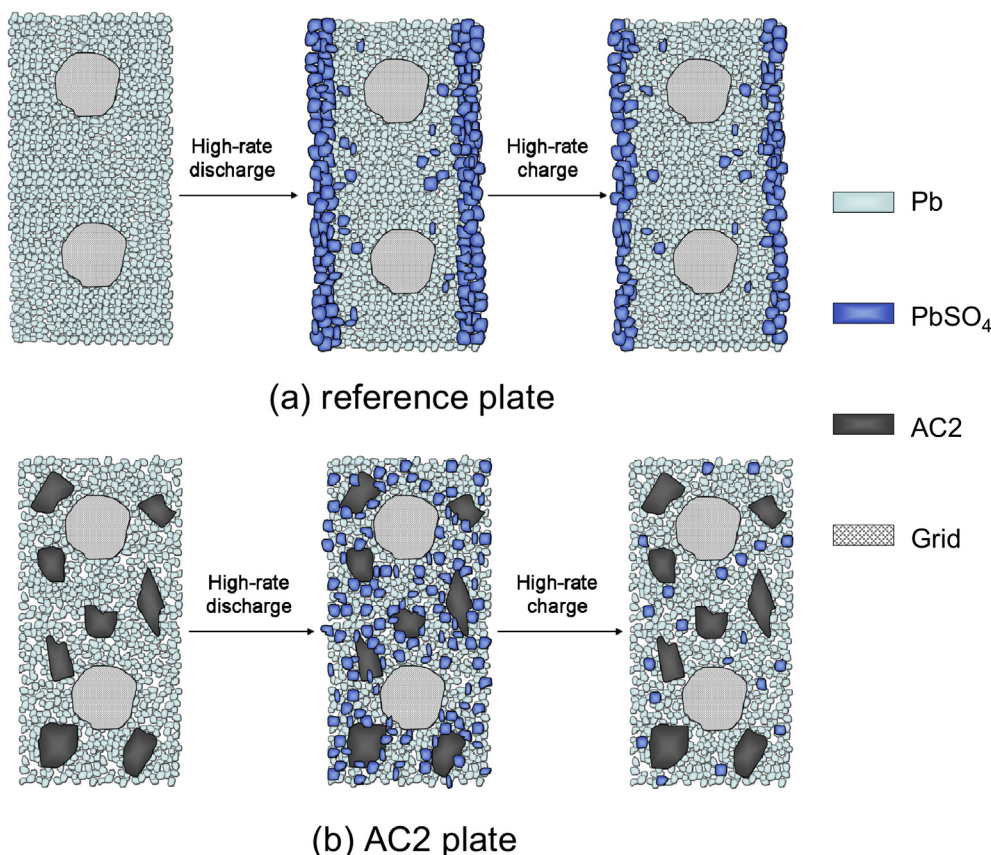


Fig. 9. Schematic diagram for electrolyte-supplying effect of activated carbons.

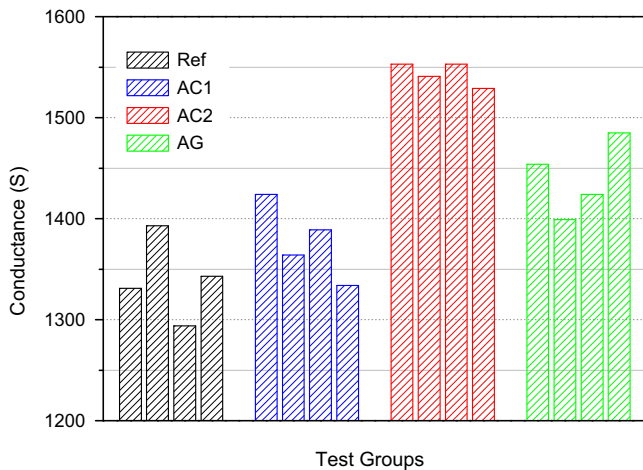


Fig. 10. Conductance data for 4 batteries of test groups: reference, AC1, AC2 and AG, respectively.

these two cells are the same. The charge and discharge mode is identical to the simulated HRPSoC profile mentioned in Section 3.1. Current flowing through the parallel-connected lead and carbon electrodes is presented in Fig. 11. In the initial stage of both charge and discharge, the carbon plate do share partial current from the external circuit, but the current value is much smaller by comparing to that flowing through the lead plate. Moreover, the shunting of carbon plate lasts a very short time of only about 10 s, after that, the current flowing through carbon plate decreases to nearly zero, while the lead plate assumes all the current in the circuit. The appearance of current in carbon plate instantly indicates the fast non-Faradaic charge of the $\text{PbO}_2/\text{carbon}$ pseudocapacitance, and the disappearance of current indicates the full charge of the capacitance.

It can clearly be seen the shunting contribution of a full-carbon electrode is so weak, to say nothing of the electrode with only 2 wt.% carbon in NAM. Therefore, some researchers believe that the quantity of carbon addition in negative plate is too low to exhibit notable capacitive effect no matter how high the capacitance is [7,20].

In order to further clarify whether the carbon mixed into spongy Pb make capacitive contribution to the electrode, we charged the 2 V cell with very low current at 50% SoC and recorded the open

circuit potential (OCP) of negative electrode after charge. Here we choose 0.1 C instead of 2 C, since the electrode polarization is relative small at low rate, which means the deviation of electrode reaction potential from the equilibrium potential is smaller. However, if charged at high rate, the electrode polarization becomes larger, thus the self-depolarization process after charging would cover the additional reaction information of the electrode.

Fig. 12 shows the significant difference of OCP changing trend between the reference and AC2 electrodes after low-rate charge. For pure lead electrode, the OCP quickly returns to an equilibrated potential of -0.962 V and keeps stable in the following 300 s. But, the OCP of AC2 plate with 2 wt.% carbon additives changes much more slowly and become stable after 20–40 s. The slow stabilizing process suggests there are still some reactions occurring in electrode even after the current is cut off. The most possible reaction should be the transformation of PbSO_4 to Pb that promoted by the charge released from the double-layer capacitance of activated carbon.

The schematic diagram for capacitance effect of activated carbon is represented in Fig. 13. The large BET surface of activated carbon can form large area of electric double layer, which is able to store protons and electrons very rapidly in high-rate charge and discharge conditions. Therefore, during HRPSoC cycling, Faradaic phase transition of Pb/PbSO_4 and non-Faradaic charge adsorption and desorption proceed simultaneously in the negative electrode. Supposing the phase transition between Pb and PbSO_4 is equivalent to electric component “R”, and the charge adsorption and desorption is equivalent to electric component “C”, the AC2 negative electrode can be treated as thousands of parallel R–C micro-circuit. Taking the high-rate charge process as an example, at the initial moment, the activated carbon acts as an effective peak power buffer accepting much of the transient current which would otherwise lead to hydrogen evolution (Fig. 13a). As the discharge time increases, the capacitor is fully charged, the external circuit then delivers more and more electrons for phase transformation from PbSO_4 to Pb. Accordingly, the current flowing through the non-Faradaic part decreases even to zero (Fig. 13b). The Faradaic part of the cell can cope with events that take place over a longer timescale. When charge is completed, the external circuit no longer provides electrons to the micro-cells. At this time, the electrons stored in the electrical double layer on the active surface of carbon then release and keep on supplying electrons for electrode reaction within a certain time. That’s why the OCP of AC2 plate decline more slowly than that of pure Pb plate after charge is cut off.

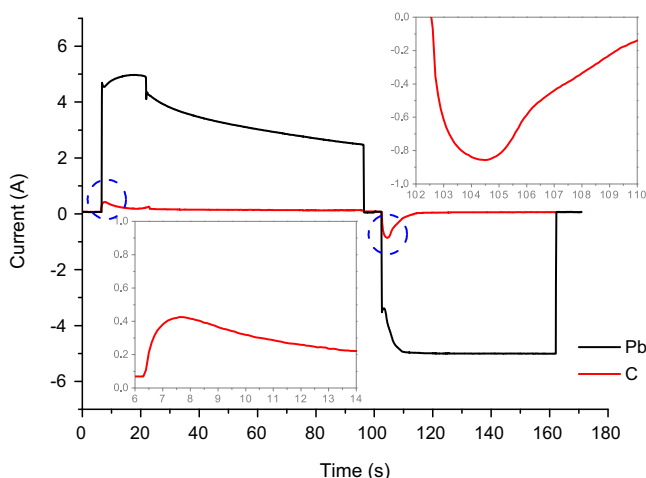


Fig. 11. Current flowing through the parallel-connected lead and carbon electrodes.

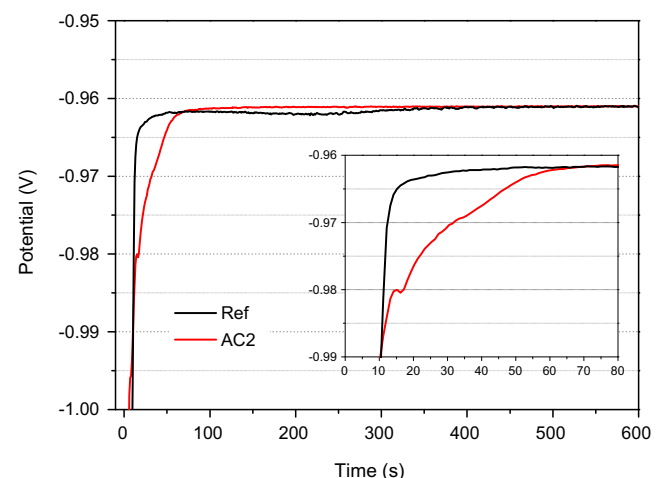


Fig. 12. Open circuit potential of negative electrodes after 0.1 C charge.

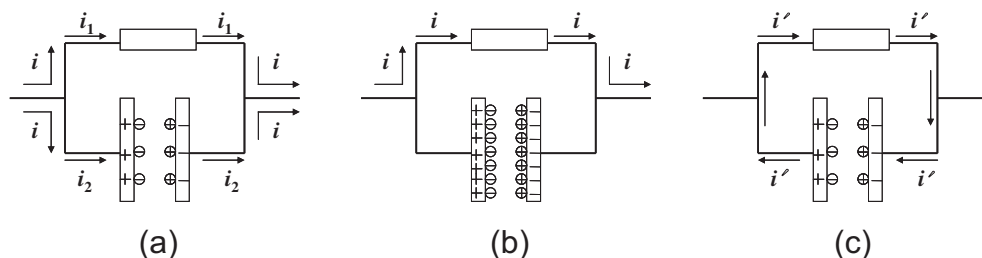


Fig. 13. Schematic diagram for capacitive-buffer effect of activated carbons: (a) initial stage of charge; (b) steady stage of charge; (c) the stage after charge.

Therefore, the capacitive-buffer effect of carbon additives in NAM should be existed though the impact might be a little tiny. The activated carbon shares the discharge and charge peak currents with the lead-acid negative plate, and thus prevents NAM from insufficient electrochemical conversion at high rate.

5. Conclusions

Prolonged HRPSOC cycle life and enhanced charge acceptance is achieved by adding 2 wt.% as-designed activated carbon with tens of micron in diameter into NAM. For contrast, negative plates with 2 wt.% activated carbon particles with much smaller size of several microns and that without activated carbon are also prepared. Based on the research of NAM microstructures and electrochemical properties of the 2 V cells and 12 V batteries, the functions of activated carbon responsible for the improved HRPSOC performance are illustrated as: prolonged HRPSOC cycle life and enhanced charge acceptance are achieved by adding 2 wt.% as-designed activated carbon with tens of micron in diameter into NAM. For contrast, negative plates with 2 wt.% activated carbon particles with much smaller size of several microns and that without activated carbon are also prepared. Based on the research of NAM microstructures and electrochemical properties of the 2 V cells and 12 V batteries, the roles of activated carbon responsible for the improved HRPSOC performance are illustrated as: (i) “new porous-skeleton builder” that increases the porosity and BET surface of NAM, facilitating electrolyte diffusion from surface to inner and providing more sites for crystallization and dissolution of lead sulfate; (ii) “inner electrolyte supplier” that provides sufficient H_2SO_4 , which is stored in the large quantity of mesopores of carbon, when the diffusion of H_2SO_4 from plate surface to inner cannot keep pace of the electrode reaction; (iii) “capacitive buffer” that absorbs excess charge current which would otherwise lead to insufficient NAM conversion and hydrogen evolution.

According to the above viewpoints, the appropriate activated carbon additives should have these characteristics: (i) large particle size of tens of micron and good affinity with lead and lead sulfate to build up a stable and highly porous skeleton in NAM; (ii) high BET surface area and porosity to store abundant electrolyte in its mesopores, supplying H^+ and HSO_4^- in the inner of plate when the diffusion of H_2SO_4 from outside is delayed; (iii) high capacitive activity to shunt excess charge current, preventing the negative plate from being discharged and charged at high rate. It is noted that, optimum carbon additives should not be limited to this kind of activated carbon. The mixture of activated carbon with carbon black or graphite might arouse new functions by the interaction of each

group, thus leading to even better HRPSOC performance. Moreover, the negative impact on hydrogen over-potential by introducing carbon additives also needs to pay close attention.

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